7th Int. Symp. "Nanostructures: Physics and Technology"
St Petersburg, Russia, June 14–18, 1999

Granulated metallic nanostructure fabricated by laser ablation

V. M. Kozhevin, D. A. Yavsin, S. A. Gurevich, V. M. Kouznetsov,
V. M. Mikushkin, S. Yu. Nikonov, A. N. Titkov and A. V. Ankudinov
Ioffe Physico-Technical Institute, St Petersburg, Russia

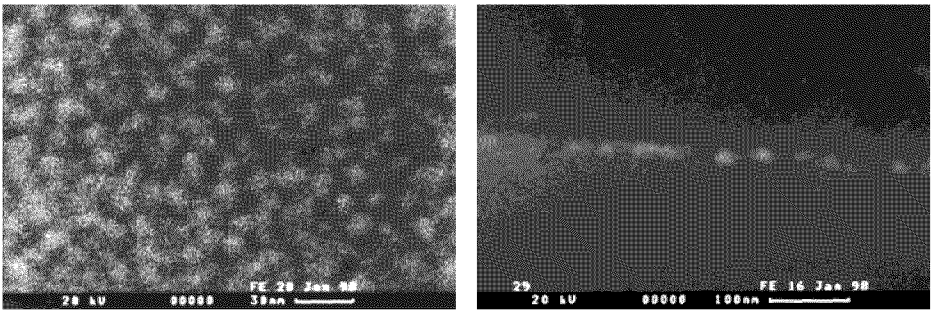
Abstract. A new method for the fabrication of monodisperse metallic nanostructures is described. The method is based on laser ablation of Cu target and subsequent fission of the splashed liquid Cu drops resulting from drops charging in the laser torch plasma up to instability threshold. The monodisperse charged nanoparticles produced by fission are directed to the substrate by the external electric field. The final stage of structure formation is free air oxidation of the deposited film. The structures were studied by SEM, AFM, surface profilometry, and XPS methods. It is shown that the film consists of closely packed spherical Cu nanoparticles, about 6 nm in diameter, covered by the Cu_2O layer of the thickness of 0.8 nm. Average gap between the neighbouring nanoparticles is controlled by laser beam intensity and it can be changed from $\delta x \approx 1$ nm to $\delta x \approx 4$ nm. The fabricated films can consist of one or several monolayers of oxidized Cu granules.

Introduction

The fabrication of granulated metallic nanostructures has gained considerable attention because of their potential use for designing of novel types of electronic devices. In particular, such structures are promising for fabrication of single-electron devices operating at elevated temperatures [1]. To fabricate these devices one needs to produce monodisperse metallic granules with typical size less then 10 nm. For this it would be necessary to use either a nm-resolution lithography or to use a source of nanoparticles together with manipulation techniques, allowing for proper particle positioning, or to employ nanoparticles self assembling. These techniques could not be referred as well developed ones, therefore, novel approaches towards nanostructure fabrication and manipulation are needed. We report on novel method of granulated nanostructure fabrication based on laser ablation of metallic target and discuss the results of this structure studies.

1 The method of structure formation

The experimental structures were fabricated using the method described previously in [2]. This method is based on laser ablation of metallic target with further fission of splashed liquid metallic drops in laser torch plasma. The beam from pulsed AIG Nd^{3+} laser was introduced into the vacuum chamber through the side port and focused on the Cu target to produce the power density about 10^9 W/cm^2. The vacuum chamber was pumped down to 10^{-5} Pa. Illumination of the target by intense laser beam results in surface heating, melting, and evaporation of the target material. In the laser torch, besides of ionised Cu vapours, liquid Cu drops of submicron size arise due to instability of the melt surface layer. These drops get charged in plasma and, if the plasma electron temperature is high enough, became to be unstable [3]. The analysis shows that the electron temperature should be as high as 60 eV to generate capillary instability of the drops and to produce their subsequent fission. The process of drop fission is of cascade type and it stops when the drop size reduces down to the critical value, $d_{\text{crit}} \approx 10$ nm. This critical size is determined by autoelectronic charge



(a) (b)

Fig. 1. SEM image of fabricated monolayer. (a) plain view and (b) cross view.

emission from the surface of the drop. As a result, relatively big initial drops with wide size dispersion turn on the set of nearly monodisperse nanoparticles. The nanoparticles formed near the target are still charged and thus their movement can be controlled by the external electric field. To collect nanoparticles on the substrate the DC voltage (1–3 kV) was supplied between the target and the anode where substrate was fixed. It is to note that the above voltage was not enough to direct the big drops to the substrate. In this way the additional mechanism for the particle size separation was realised.

The particles were deposited on the alumina, silicon, and oxide-passivated silicon substrates. The final stage of the process was free air oxidation of the nanostructure. The described method allows to fabricate films which consist of one or several monolayers of the nanometric granules and, what is more, the number of monolayers is controlled by the process duration. Below, we discuss the results of structure studies of oxidized granulated films.

2 Experimental results and discussion

Fig. 1(a) shows the SEM plain view of the fabricated granulated film. As one can see in this figure, the granules are closely packed and the characteristic size of individual granules can be estimated as 10 nm. Analysis of SEM images of the structures obtained under different conditions, at different values of the laser beam intensity, showed that the nanoparticles of about 10 nm in diameter exist only if laser beam intensity exceeds certain critical value I_{cr}. Above this threshold the particles size is nearly constant.

Estimations show that experimental value of I_{cr} is just the intensity needed to heat the electrons in the laser torch plasma up to the temperature $T_e \approx 60-70$ eV. As we have mentioned above this temperature is desired to charge the initial "big" drops up to capillary instability threshold [4] and initiate drops fission. Another observation resulted from the analysis of SEM images is that the distance between the centres of neighbouring granules grows from the 8 nm to 12 nm with the increase of the laser beam intensity from I_{cr} to $2I_{cr}$. This can be explained by more intensive target evaporation in the case of more powerful laser beams. As a result, at higher laser pulse power the deposited drops are separated by larger amount of atomic size Cu particles. Fig. 1(b) displays the cross-sectional SEM image of the film shown in Fig. 1(a) (deposition during 3 minutes, pulse repetition frequency is 28 Hz). It is clearly seen that this film consists of one monolayer of closely packed spherically shaped granules. With the accuracy provided by SEM images we can conclude that all the fabricated nanostructures are monodisperse.

The monolayer films were analysed by AFM. Experiments performed with the tip having

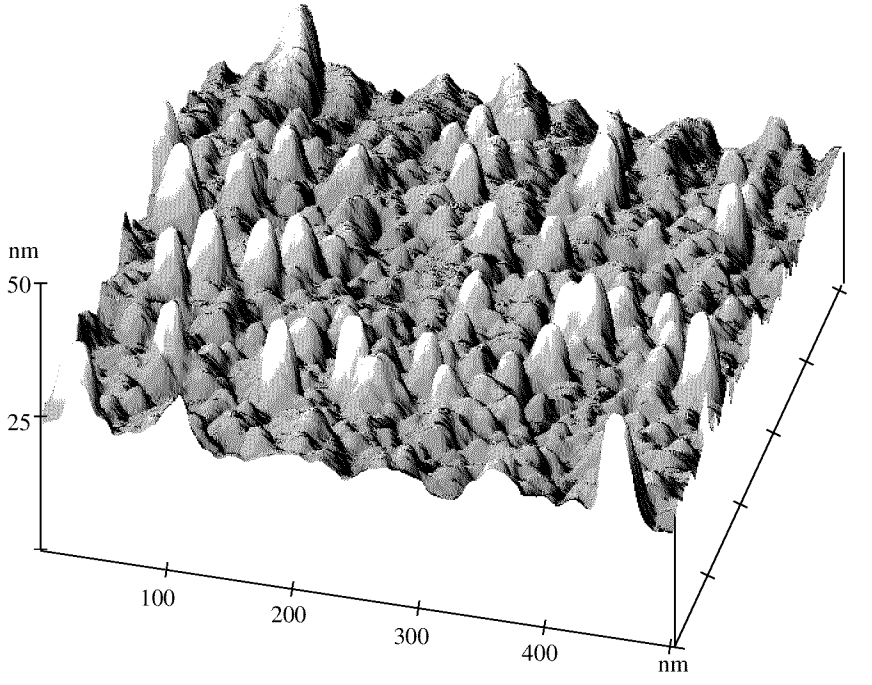


Fig. 2. AFM image of fabricated monolayer.

the end radius $\approx$ 40 nm show that the amplitude of the surface modulation is not more the 1 nm and characteristic lateral size of surface inhomogenity is about 40 nm. Using of sharper tip with the end radius $r \approx 10$ nm gives the surface modulation depth 5 nm and the size of surface inhomogenity 15 nm (Fig. 2). The results of both AFM measurements can be explained taking into account that the tip is in contact simultaneously with several closely packed granules and assuming the mean granule diameter 8 nm, which is consistent with SEM observation.

Measurements of the film thickness were done by DEKTAK profilometer. First, the strips of granulated film were formed on the substrate surface by lift-off technique. Then, to increase the structure rigidity the structure was covered by the thin SiO_2 layer. Three different samples were fabricated, keeping the laser beam intensity close to I_{cr} and varying the time of deposition: (1) 3 minutes, (2) 3 minutes deposition—30 minutes interval, four times repeated for the total deposition of 12 min., and (3) continuous deposition during 12 minutes. The measured thickness of the first film is $H_1 > 8$ nm, the second film has the thickness $H_2 > 20$ nm, and the third film thickness is $H_3 > 19$ nm. Noting that the granule size is typically 8 nm, the thickness of the first film corresponds to one monolayer of granules. The data on the second film thickness can be understood if we propose that the film consists of four layers of granules, closely packed so that in each layer the gap between the neighbouring granules is about $\delta x > 1$ nm. Comparing the data on the second and the third films one can conclude that the film thickness depends only on the total time of deposition.

The information about the chemical composition of the granulated films was obtained by using XPS measurements of monolayer films. Analysis of the photoelectron spectra shows that the film consist mainly of the copper and the oxygen. The fraction of oxygen measured

in as-made films (free air oxidized) is 16%, whereas measurements of the films pre-etched by the Ar+ ions (0.5 nm removed) give the oxygen content 10%. It should be noted that oxidized thin film can contain only Cu_2O oxide because $Cu_2 \rightarrow CuO$ reaction is possible only in the oxide layer with the thickness exceeding 250 nm [4]. To estimate the thickness of the Cu_2O layer we assumed that spherical granules are oxidized homogeneously from the surface. In this case the oxygen content 16% corresponds to the thickness of Cu_2O spherical layer $dR > 0.8$ nm. Removing 0.5 nm of the material from the upper part of the granules by surface etching results in reducing of the oxygen percentage. The experimental value of oxygen content 10% is in a good agreement with the estimation based on the assumption of homogeneous surface oxidation.

Summing up, the granulated Cu films fabricated by laser ablation consists of the monodisperse spherical Cu granules, 6 nm in diameter, covered by 0.8 nm thick Cu_2O layer. Each monolayer of such granules is closely packed. The gap between the neighbour granules depends on the deposited mass of vaporised Cu and is controlled by the laser beam intensity. This distance increases from $dx > 1$ nm for $I > I_{cr}$ up to $dx > 4$ nm for $I > 2I_{cr}$. Due to the possibility of close control of structure parameters such films are of interest for the study of transport properties of low dimensional nanostructures.

This work was supported in part by RFBR grant No 98-02-18210, the Program of the Ministry of Science of RF "Physics of Solid-State Nanostructures" grants Nos 97-2014, 97-1035, State Program "Micro- and Nanoelectronic Technology" grant 151/57/1.

References

[1] E. Bar-Sadeh, Y. Goldstein, C. Zhang, H. Deng, B. Abeles and O. Millo, *Phys. Rev.* **B50**, 8961 (1994).

[2] S. A. Gurevich, V. M. Kouznetsov, V. M. Kozhevin, D. A. Javsin, D. A. Zakheim, V. V. Khorenko and I. V. Rozhansky, 6th International Symposium *Nanosructures: Physics and Technolody*, St. Petersburg, Russia, p. 344, 1998.

[3] A. I. Grigor'ev, S. O. Shiryaeva, S. S. Verbitskii and J. Coll, *Interface Sci.* **146**, 137 (1990).

[4] B. V. Nekrasov, *Basics of General Chemistry*, Moscow, Vol. 3, p. 50, 1965.